

Channel coupling and shape resonance effects in the photoelectron angular distributions of the $3\sigma_g^{-1}$ and $2\sigma_u^{-1}$ channels of N_2

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We report measurements of photoelectron angular distributions for the $3\sigma_g^{-1}$ and $2\sigma_u^{-1}$ photoionization channels of N_2 from their thresholds up to 35 and 37.5 eV, respectively. The asymmetry parameter β for the $2\sigma_u^{-1}$ channel exhibits a broad dip in the range $h\nu \sim 27\text{--}32$ eV that was recently predicted theoretically to arise from shape-resonance-enhanced continuum-continuum coupling between the $3\sigma_g^{-1}$ and $2\sigma_u^{-1}$ ionization channels. The β parameter for the $3\sigma_g^{-1}$ channel exhibits a prominent feature at $h\nu \sim 23$ eV, which is tentatively attributed to the autoionization of a doubly excited valencelike state. Otherwise, the gross shape of the $3\sigma_g^{-1}$ β curve is in good agreement with independent-electron calculations, which realistically reflect the influence of the well-known σ_u shape resonance in this channel.

I. INTRODUCTION

The earliest measurements¹ of photoelectron angular distributions for the valence orbitals of N_2 over a broad energy range provided evidence for many-electron effects in the photoionization continuum of N_2 . In particular, Marr *et al.*¹ suggested that a broad dip in the photoelectron asymmetry parameter, β , near $h\nu \sim 32$ eV in the $2\sigma_u^{-1}$ channel, was the result of "interchannel interference." Calculations of β 's for the valence levels of N_2 have been reported by Wallace *et al.*,² using the multiple-scattering model (MSM), and by Lucchese *et al.*,³ using the frozen-core Hartree-Fock model with a correlated initial state. Both theoretical calculations agreed well with measured β 's for the $3\sigma_g^{-1}$ and $1\pi_u^{-1}$ channels, but both deviated significantly from the data for the $2\sigma_u^{-1}$ channel, particularly in the range $h\nu \sim 25\text{--}35$ eV.

In an attempt to understand the persistent differences between experiment and theory for the $2\sigma_u^{-1}$ channel, Stephens and Dill⁴ included the effects of continuum-continuum coupling with the $3\sigma_g^{-1}$ channel. They have shown that a large dip should appear in the β parameter for the $2\sigma_u^{-1}$ channel, near the photon energy at which the well-known σ_u shape resonance⁵ occurs in the $3\sigma_g^{-1}$ channel. In the independent-electron model, the $2\sigma_u$ orbital cannot access the σ_u continuum due to the parity-selection rule. However, in a many-electron picture the $(2\sigma_u^{-1})(\epsilon\sigma_g)^1\Sigma_u^+$ and $(3\sigma_g^{-1})(\epsilon'\sigma_u)^1\Sigma_u^+$ continuum channels may couple due to the electron-electron interaction. Normally, the continuum-continuum interaction is expected to be relatively weak, but Stephens and Dill have shown that the shape resonance in the $3\sigma_g^{-1}$ channel provides a mechanism for enhanced coupling. This is plausi-

ble because, in the resonant energy range, the $\epsilon'\sigma_u$ electron becomes quasibound to the molecular core,⁵ providing enhanced probability of electronic collision with and ejection of the $2\sigma_u$ electrons. Interchannel coupling effects, including enhancement due to a shape resonance, are well established in atomic photoionization.⁶

The Stephens and Dill calculation⁴ on the N_2 $2\sigma_u^{-1}$ photoionization channel appears to explain qualitatively the discrepancy between independent-electron calculations and the β measurements of Marr *et al.*¹ and, more recently, of Adam *et al.*⁷ However, the experimental evidence is sparse. Here we present a new set of β measurements for $N_2^+(2\sigma_u^{-1})B^2\Sigma_u^+$, $v'=0$, obtained for $h\nu=19.5\text{--}37.5$ eV with sufficient point density to establish clearly the profile of the β parameter. We obtain a distinct, broad minimum in the range $h\nu=27\text{--}32$ eV, which appears to confirm qualitatively the prediction of shape-resonance-enhanced, continuum-continuum coupling. The measurements are not in quantitative agreement with the calculation of Stephens and Dill, thus providing impetus for further theoretical work to resolve the residual differences. These results are also consistent with and complement evidence from fluorescence excitation⁸⁻¹⁰ and partial-cross-section measurements^{10,11} which also suggest deviations from independent-electron behavior for this channel.

We also report β measurements for $N_2^+(3\sigma_g^{-1})X^2\Sigma_g^+$, $v'=0$, obtained over the range $h\nu=16\text{--}35$ eV. Those results reflect two important contributions to the photoionization dynamics of N_2 . The first is the σ_u shape resonance occurring near 29 eV which has been extensively studied in this and other observables.⁵ The second is the interaction with doubly excited states in the region of 23 eV.^{8,9,12-15}

II. EXPERIMENT

The measurements were performed at the Synchrotron Ultraviolet Radiation Facility at the National Bureau of Standards, Gaithersburg, Maryland. A high-throughput, normal-incidence monochromator¹⁶ was used with a 2400-line/mm osmium-coated grating, blazed for 500 Å in first order. The bandpass of the monochromatized light was 0.9 Å full width at half maximum (FWHM). The intensity of the light was monitored with tungsten photodiodes, and the degree of polarization was measured using a triple-reflection analyzer. The polarization was typically 70–75 %.

The electron-spectrometer system was a second-generation instrument designed for high-resolution, angle-resolved studies.¹⁷ The system contains two 10.2-cm-mean-radius hemispherical electron analyzers, one of which is fixed to accept photoelectrons ejected at 0° with respect to the major polarization axis of the light beam, while the other analyzer is rotatable. In the present experiment, the rotatable electron analyzer was held fixed at 90°. The photoelectron asymmetry parameters, β 's, were determined from the relative intensities of photoelectrons detected at 0° and 90°, after suitable calibration procedures. The electron analyzers were operated at 10 eV pass energy which, in combination with the photon bandpass, resulted in an electron-energy resolution in the range 90–130 meV FWHM. This was sufficient to resolve vibrational structure in the photoelectron spectrum of N₂.

The transmission functions and angular calibration were determined over the kinetic-energy range of 0–20 eV by measurements on Ne, Ar, Kr, and Xe for which the angular asymmetry parameters¹⁸ and total cross sections¹⁹ are known fairly well. A complete discussion of calibration and data-analysis procedures is given in a separate paper.²⁰ As noted there, the largest uncertainty occurs for electron kinetic energies greater than 10 eV, owing to less-well-characterized β standards and the existence of autoionization structure in the rare gases which was unresolved with the bandpass used in the present arrangement. These difficulties notwithstanding, the calibration procedure was found to be internally consistent among the rare gases and is believed to be accurate within stated error bars. Calibration data sets were recorded frequently in order to check the stability of the spectrometer system. The relative collection efficiencies of the two electron analyzers were found to be stable over a period of several months, during which measurements of molecular gases were interspersed with measurements on the rare gases.

Studies were also conducted to check for pressure effects which can arise due to photoelectron scattering from the sample gases. For each sample gas the photoelectron intensity detected in each analyzer was measured as a function of pressure at or near the maximum of the scattering cross section.²¹ From those measurements an appropriate pressure range was indicated over which the angular distribution measurements were free of significant scattering effects. In addition, several of the N₂ data points were recorded at different pressures as a check for possible scattering effects.

III. RESULTS AND DISCUSSION

The present results for the β parameter for N₂⁺ ($2\sigma_u^{-1}$)B² Σ_u^+ , $v'=0$, are shown in Fig. 1, along with previous vibrationally averaged data^{1,7} and three theoretical curves.^{2–4} We discuss the theoretical curves first in order to indicate the qualitative nature of the physical effect in which we are interested. The dashed curve is the single-channel multiple-scattering model (MSM) result,² representing the behavior predicted in the independent-electron, fixed- R , local exchange approximation in a MSM model potential. The solid line represents the Hartree-Fock (HF) result of Lucchese *et al.*,³ which includes initial-state correlation in addition to intrachannel coupling in the final state. This calculation improves both the initial state and the final state, but still neglects coupling between alternative ionization channels. These two calculations differ in detail, but they show the same qualitative behavior; namely, a monotonic increase from threshold toward higher energy. As the HF result is more accurate, we will use it in what follows to represent the independent-electron level of approximation. As indicated in the Introduction, the failure of early measurements¹ to reproduce this trend stimulated Stephens and Dill to incorporate continuum-continuum coupling between the $2\sigma_u^{-1}$ and $3\sigma_g^{-1}$ ionization channels in anticipation of a transfer of shape-resonant behavior from the $3\sigma_g^{-1}$ resonant channel to the nominally nonresonant $2\sigma_u^{-1}$ channel. Their results are indicated in Fig. 1 by the open circles, connected by a solid line. These results show that coupling the two channels induces a dramatic dip in the β parameter at about 34 eV. This dip occurs at the photon energy of the σ_u shape resonance in the $3\sigma_g^{-1}$ channel in the MSM-model calculation used to generate the one-electron basis for the K -matrix calculation. The experimental energy of the shape resonance in the $3\sigma_g^{-1}$ channel is, of course, near $h\nu \cong 29$ –30 eV. (The MSM calculation

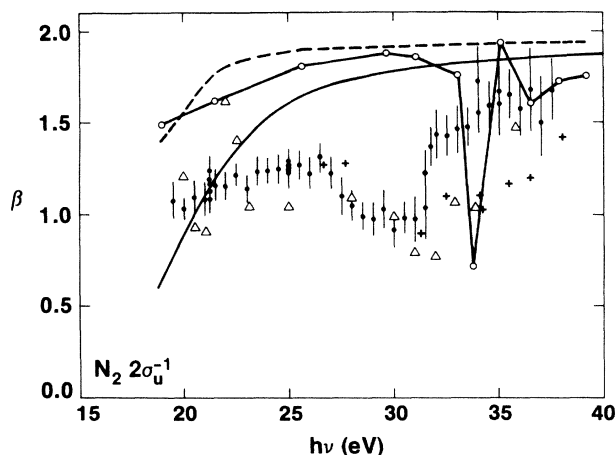


FIG. 1. Photoelectron asymmetry parameter for N₂⁺ ($2\sigma_u^{-1}$)B² Σ_u^+ . Solid circles, present measurements for $v'=0$; triangles, vibrationally averaged measurements from Ref. 1; pluses, vibrationally averaged measurements from Ref. 7; dashed line, single-channel MSM calculation from Ref. 2; solid line, HF (dipole-length form) calculation from Ref. 3; open circles with line, two-channel MSM calculation from Ref. 4.

could have been altered to reproduce this energy exactly, but this is usually not done, as no new information is obtained and there is no point in exaggerating the accuracy of the method.) Note that, on either side of the shape-resonance-induced feature, the two-channel result behaves much like the single-channel result, indicating that strong continuum-continuum coupling is mediated by the shape resonance.

The present results are shown as solid dots in Fig. 1. They show clearly the shape of the $2\sigma_u^{-1}$ β parameter in this spectral range. In particular, the present data exhibit a clear broad minimum near the photon energy of the σ_u shape resonance in the $3\sigma_g^{-1}$ channel. The width is also close to the σ_u shape resonance width. These observations qualitatively confirm the shape-resonance-induced continuum-continuum coupling mechanism invoked by Stephens and Dill. The minimum is at lower energy and is broader than the two-channel calculation. The shift traces mainly to the location of the shape resonance in the independent-electron-model calculation. The differences in shape, and to some extent the location, also arise from other approximations inherent in the prototype calculation, e.g., neglect of vibrational effects. The data converge to the HF results at energies above and below the shape resonance feature, indicating the return to essentially single-channel behavior in the absence of shape-resonance-enhanced interchannel coupling. It is important at this point to perform a coupled-channel calculation that includes vibrational effects and that would therefore produce a vibrationally resolved $v'=0$ result equivalent to the present measurement. For completeness, we also note here that deviations from independent-electron behavior for the $2\sigma_u^{-1}$ channel could, in principle, arise from interaction with excited states associated with the inner-valence ionization spectrum.²² While this alternative mechanism could play some role, the model of Stephens and Dill appears adequate to explain the essential aspects of the present observations. This question should be considered in future theoretical work.

The present results are consistent with earlier experimental evidence: previous fluorescence-excitation⁸⁻¹⁰ and partial-cross-section^{10,11} measurements exhibit a weak, broad peak in the $2\sigma_u^{-1}$ partial cross section in the $h\nu=28-35$ eV region. This is suggestive of shape-resonance-induced transfer of oscillator strength from the $3\sigma_g^{-1}$ channel to the $2\sigma_u^{-1}$ channel, in accordance with the continuum-continuum coupling mechanism. This enhancement occurs over roughly the same energy region as the dip in the β parameter, and does not occur in independent-electron treatments. The earlier measurements by Marr *et al.*¹ and by Adam *et al.*⁷, were, of course, the first indications of many-electron effects in the β for the $2\sigma_u^{-1}$ channel; however, those data were too sparse to clearly establish the profile of the spectral dependence of β . The present data are qualitatively consistent with the earlier measurements and, in addition, define the profile of the β curve clearly. Some deviations do exist among the data sets, however. (In making these comparisons, note that the uncertainties in the data by Marr *et al.*¹ were typically ± 0.15 β units. The uncertainties in the data by Adam *et al.*⁷ were not shown, but are

assumed to be roughly similar to the other two data sets.) At low energy the data by Marr *et al.*¹ show scatter not present in the present data. This could be due to autoionization structure, although the earlier data was taken with 3–8 Å photon bandpass and should therefore be less sensitive to sharp spectral structure than the present data taken with 0.9 Å bandpass. Also, e -N₂ scattering has a high cross section which could affect β measurements in this region, an effect carefully eliminated in the present work. Another deviation occurs in the $h\nu=32-36$ eV range, where the present data are consistently higher than earlier data. This is a region of greater uncertainty in our calibration procedure, as mentioned in the preceding section, but we believe the present data are accurately calibrated to within stated error bars. Finally, we repeat that the present data are vibrationally resolved results for $v'=0$, whereas the earlier data are vibrationally averaged. As the $v'=0$ has the largest Franck-Condon factor ($\sim 90\%$), this will not be an important difference for *nonresonant* processes. In resonant processes, however, weak vibrational channels can be enhanced and may account for some of the observed differences. This should be investigated in future work.

In Fig. 2 are plotted the present measurements for N₂⁺ ($3\sigma_g^{-1}$)X²Σ_g⁺, $v'=0$, along with the $v'=0$ data of Carlson *et al.*,²³ the MSM calculation of Dehmer *et al.*,²⁴ and the HF calculation of Lucchese and McKoy.²⁵ Both theoretical curves are specifically for the $v'=0$ vibrational level and were obtained using the adiabatic nuclei approximation. We obtain good overall agreement with the data of Carlson *et al.*,²³ with the $v'=0$ measurements of Holmes and Marr,²⁶ and with the vibrationally averaged measurements of Marr *et al.*¹ For clarity of viewing, the latter two data sets are not plotted in Fig. 2.

The present data for the $3\sigma_g^{-1}$ channel were obtained originally as a check on our experimental technique in order to gain confidence in the results for the $2\sigma_u^{-1}$ channel.

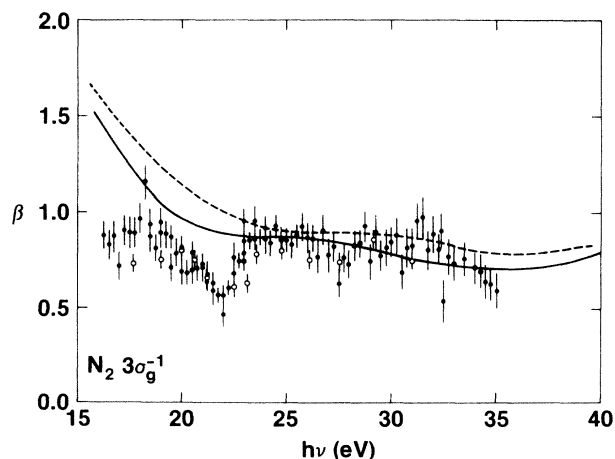


FIG. 2. Photoelectron asymmetry parameter for N₂⁺ ($3\sigma_g^{-1}$)X²Σ_g⁺, $v'=0$. Solid circles, present measurements; open circles, measurements of Ref. 23; dashed line, MSM calculation from Ref. 24; solid line, HF (dipole-length form) calculation from Ref. 25.

However, the $3\sigma_g^{-1}$ data set is of interest in itself, as it clearly reveals the shape of the β curve in this important spectral range. The data exhibit the same absolute value but slightly more spectral variation than the theoretical curves indicate in the region of the broad σ_u shape resonance. This resonance is centered at $h\nu \sim 29$ eV, but it affects the β parameter over a broader spectral range than its ~ 5 eV FWHM.²⁴ Its main effect is to produce a significant ν' dependence in β , as discussed elsewhere.^{23,24} Not plotted in Fig. 2 are two recent theoretical curves obtained in the fixed-nuclei approximation.²⁷ The theoretical curves^{24,25,27} differ in minor ways among themselves for the shape and magnitude of β in the shape resonance region; however, the shapes of the theoretical curves in Fig. 2 are indicative of the current status of theory for this channel.

To date, no theoretical calculation has reproduced the strong, broad dip in β observed around 20–23 eV. This feature was also obtained in the measurements by Carlson *et al.*²³ and by Holmes and Marr.²⁶ Similarly, broad structure near 23 eV has been observed in the partial photoionization cross section for $3\sigma_g^{-1}$.²⁸ Spectral features observed near 23 eV have often been attributed to channel interaction involving Rydberg series¹² leading to the doubly excited N_2^+ ($3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^{-1}$) $C^2\Sigma_u^+$ state. However, while sharp Rydberg-like structure has been observed near 23 eV (see, e.g., Refs. 8, 9, 12, 13, and 15), the structure observed here in the $3\sigma_g^{-1}$ β parameter and in the $3\sigma_g^{-1}$ partial cross section²⁸ is quite broad. These observations

are compatible since the photoabsorption cross section near 23 eV exhibits weak, sharp structure superimposed on a broad maximum.^{13,15} Wendin has suggested¹⁴ that the broad structure arises from a doubly excited, valence-like state represented by ($3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^{-1}$). This proposed doubly excited, valence-like state would have a very short lifetime, resulting in broad spectral structure more like the observed feature than the sharper Rydberg structure mentioned above.

In conclusion, we have observed a prominent dip in β for the $2\sigma_u^{-1}$ photoionization channel of N_2 which supports the prediction⁴ of shape-resonance-enhanced continuum-continuum coupling. We have also observed the spectral variation in β for the $3\sigma_g^{-1}$ channel in the vicinity of the one-electron σ_u shape resonance and a prominent dip near $h\nu \sim 23$ eV which is attributed to interaction with a proposed¹⁴ doubly excited, valence-like state. We hope that these data will help stimulate further development of many-electron theoretical approaches to molecular photoionization.

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